Extended Surfactants Using HLDN approach

Subjects: Nanoscience & Nanotechnology

Contributor: Ana Forgiarini , Ronald Marquez , Jean-Louis Salager

Extended surfactants are molecules including an intramolecular extension that allow attaining high performance without the need for cosurfactant or linker alcohol. The polypropylene oxide chain intramolecular extension generates a polarity transition inside the molecule that produces more interactions with the oil and aqueous phases. The idea was developed in the 1990s, basically to fasten together the rather hydrophilic surfactant and the lipophilic linker, producing the same effect as the mixture without losing a part of the lipophilic linker going away from the interface. Since the lipophilic linker was an amphiphile with a small hydrophilic part located close to the interface, the single structure was developed to imitate the mixture situation. It contains a polar head located in water, then an intermediate slightly polar zone in the oil phase close to the interface, and finally, the surfactant classical hydrocarbon tail.

formulation normalized hydrophilic–lipophilic deviation HLDN extended surfactant
solubilization enhanced oil recovery interfacial tension

1. Introduction

The synthesis of surfactants for the solubilization of complex oils, including crude oils and polar oils, has been widely researched since the late 1970s [1][2]. After petroleum sulfonates were introduced [3][4][5], it was necessary to develop high-performance surfactants with reasonable production costs to advance surfactant flooding processes. Henceforth, ethoxylated oleyl sulfonates (EOS) were introduced [6][7] as the first surfactants that presented an extension from the usual alkyl chain—sulfate head surfactants. The first EOS surfactants had 2-3 ethylene oxide groups in their structure, which allowed a somewhat higher performance, although still with the need of cosurfactants to achieve high solubilizations and low IFT [6]. They were tried with long-chain hydrocarbons as the oil phase, e.g., hexadecane and paraffin oils [6][7]. Then, an additional intramolecular extension with four polypropylene oxide (PO) groups was added to sulfate surfactants [8], which allowed attaining high performance without the need for cosurfactant alcohol. This was a significant advancement in the simplification of the system, using an innovative solution, i.e., including a PO-EO intramolecular extension to generate the polarity transition inside the molecule that produced more interactions with the oil and aqueous phases. A summary and classification of the sulfate head extended surfactants developed since 1992 with the reported surfactant classification parameter (SCP_N) [9][10][11] is presented in **Table 1**. Nevertheless, other molecules have been developed with different types of polar heads (carboxylate, xylitol, glucose derived, ethoxylated nonionic), as summarized in the 2019 review [2].

Table 1. Molecular structure and classification of sulfate head extended surfactants according to its normalized characteristic parameter (SCPN) [2]

Extended Surfactant [1]	σ	k	$SCP_N = σ/k$ *	Author and Year	Ref.
$S/12/6/2/SO_4$	−1.43	0.075	−19.1	Miñana-Perez, 1995	[13]
$S/12/10/2/SO_4$	−0.3	0.11	−2.7	Miñana-Perez, 1995	[13]
$S/12/14/2/SO_4$	1.21	0.16	7.6	Miñana-Perez, 1995	[13]
$A/14{-}15/8/0/SO_4$	0.16	0.13	1.2	Witthayapanyanon, 2006	[30]
$A/10/18/2/SO_4$	0.57	0.053	10.8	Do, 2009	[39]
$A/14{-}15/4/0/SO_4$	−0.18	0.11	−1.6	Velásquez, 2010	[24]
$A/16{-}17/4/0/SO_4$	−0.29	0.11	−2.6	Velásquez, 2010	[24]
$A/12{-}13/8/0/SO_4$	−0.52	0.08	−6.5	Velásquez, 2010	[24]
$A/12{-}13/4/0/SO_4$	−0.98	0.11	−8.9	Velásquez, 2010	[24]
$Chen/8/9/3/SO_4$	−0.39	0.17	−2.3	Chen, 2019	[79]
$A/12{-}13/4/0/SO_4$	−1.55	0.049	−31.6	Wang, 2019	[41]
$He/13/2/0/SO_4$	−1.8	0.056	−32.1	He, 2019	[42]
$A/10/4/0/SO_4$	−2.24	0.053	−42.3	Phaodee, 2020	[29]

[1] Nomenclature: A: Alfoterra, S: Seppic, Chen and He are first authors of the papers where these surfactants were synthetized. A/10/18/2/S stands for Alfoterra/C10/PO18/O2/SO4. This is the same nomenclature as [2].

* SCPN is the surfactant classification parameter. Higher SCPN indicates a more important lipophilic part of the molecule (hydrocarbon tail and PO extension), a lower SCPN (more negative) indicates a more important hydrophilic head contribution.

ation with conventional surfactants, led to trying these new molecules. The polar oils tested included perchloroethylene oil [12] and ethyl oleate [13] with a (surprising at the time) very high performance. Miñana et al. [13] also tried the solubilization of triglycerides (which at the time was practically zero with conventional surfactants, even with cosurfactant alcohols) with $C_{12}PO_nEO_2SO_4$ (n = 6, 10 or 14), showing for the first time high solubilization of these bulky polar oils. In the same year, Aoudia et al. [14] achieved high performance with crude oils and a very long PO = 15 extension in a $C_{14}PO_{15}SO_4$ surfactant. These first state-of-the-art extended surfactants synthetized and proved for high solubilization of polar oils allowed a progressive advance of research [15][16]. Nevertheless, it was not until the early 2000s that new molecules were developed at FIRP Lab. [17][18][19][20], including surfactants with a carboxylate head and others derived from triglycerides and natural sugars [21][22]. These first trends concerning new extended surfactants for the high solubilization of polar oils allowed the progressive advance of research [2][20][23].

Several other surfactants that were tried since 1995 were used in different applications, including EOR and the solubilization of polar oils [24][25][26][27][28][29][30], but also other not-so-conventional applications, such as drilling fluids [31][32][33] and crude oil dewatering [34][35][36].

2. Historical Introduction on Formulation Concepts

It can be said that a century ago, the so-called Bancroft's rule and its related research and development discussions [37][38][39] were the first attempt to attain a generalized practical approach for surfactant–oil–water (SOW) systems. However, it was only in the late 1950s that two researchers from industry tried to improve the practical aspects related to SOW systems.

Griffin [40] introduced the so-called hydrophilic-lipophilic balance parameter, called HLB. Sometime later [41], he proposed several numerical expressions to estimate the HLB number as a function of the chemical structure of nonionic surfactants, e.g., 20% of the polyoxyethylene weight for an ethoxylated alcohol. HLB was related to the surfactant effect and was thus the first numerical scale that could help compare cases and averaging effects. Even though it did not take into account the effect of other variables, it was the unique numerical criterion for 25 years because it was an extremely simple concept. Thus, it is still currently used as approximate information for people in the industry who do not require high accuracy in formulation work [42].

At the same time, but in a completely different research area, Winsor [43] proposed a complex model based on the ratio R of interactions between the surfactant adsorbed at the interface and the neighboring oil and water molecules on both sides of it, indicated explicitly as A_{CO} and A_{CW} in **Figure 1**.

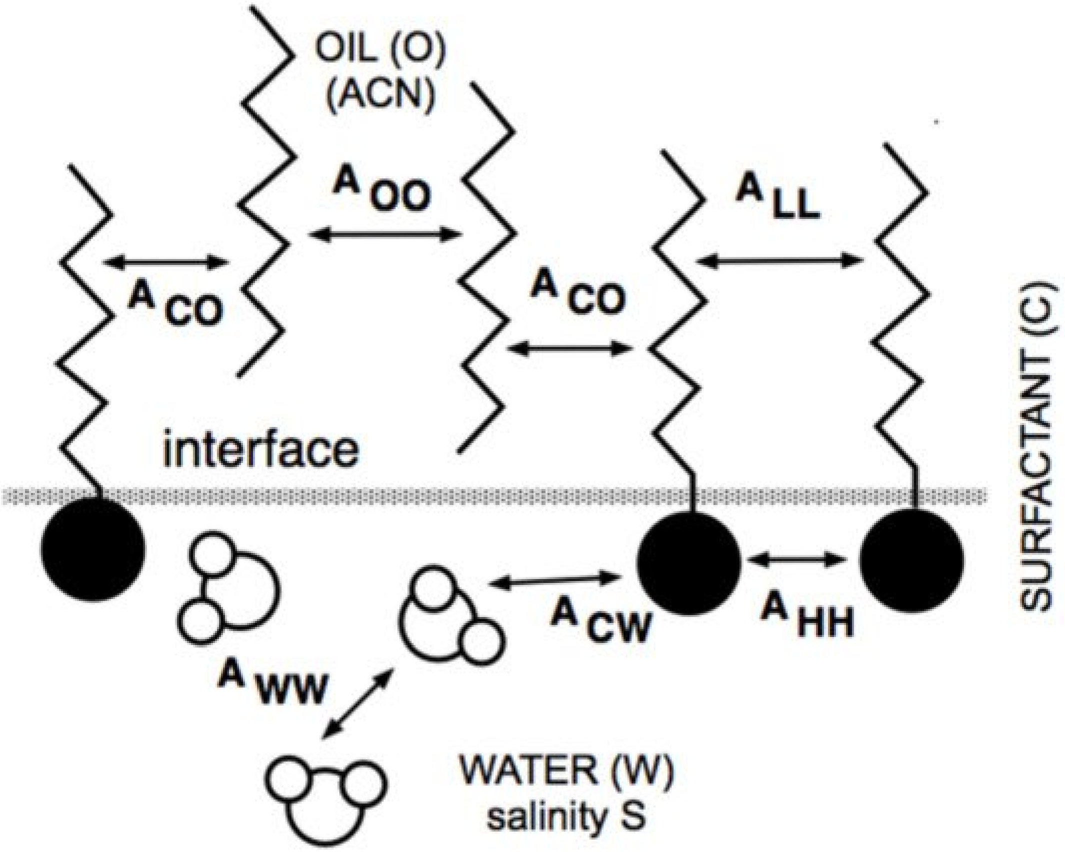

Figure 1. Interaction of surfactant, oil and water molecules close to interface according to Winsor's scheme.

The original model $R = A_{CO}/A_{CW}$ was made more realistic by introducing the self-interactions between the surfactant, oil and water molecule as references, each in separated terms [44][45].

Thus, this more precise approach resulted in a new definition of the interaction ratio as R = $(A_{CO} - A_{OO} - A_{LL})/(A_{CW} - A_{WW} - A_{HH})$, which is not discussed here because it is out of the scope of this review. Nevertheless, and as has been explained elsewhere [11][46][47][48], it must be noted that the effective interaction between the surfactant and the oil molecules, i.e., the numerator of R, tends to decrease when the oil ACN increases. This happens because A_{OO} (between two *n*-alkane molecules) increases, in general, faster than A_{CO} (between the surfactant tail and an oil molecule), while the other terms are unaltered. In what follows, R is taken as $(A_{CO} - A_{OO})/A_{CW}$ for simplicity.

The Unidimensional Scan of a Formulation Variable

In his research in the late 1940s, Winsor proposed a basic method to study a surfactant–oil–water (SOW) system by determining its phase behavior versus a continuous variation (called a scan) of a variable susceptible to alter at least one of the interactions [44]. In simple systems, these variables typically were the oil nature (e.g., the *n*-alkane carbon number ACN), the water NaCl salinity (S), the surfactant and co-surfactant type (head or tail nature), the temperature, and eventually the pressure [49][50][51], which is an essential variable in a petroleum reservoir.

Winsor reported that a three-phase behavior (central diagram in **Figure 2** left part) was occurring exactly at R = 1 and was associated with a low interfacial tension, indicated as γ* in **Figure 2**, right part.

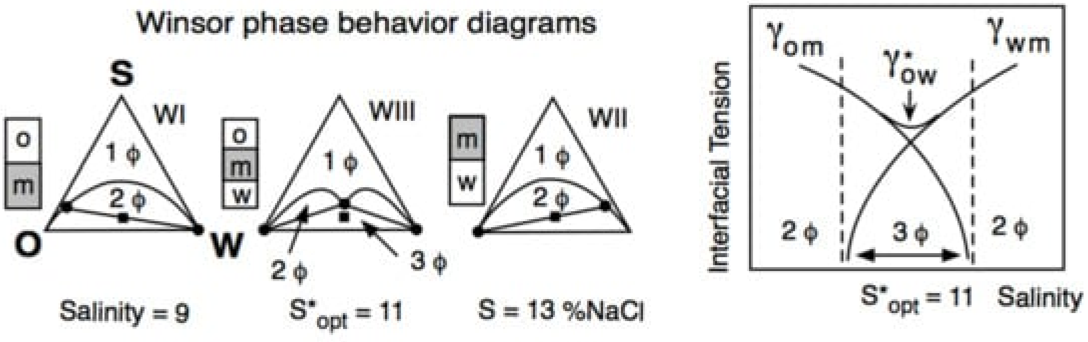

Figure 2. Variation of the interfacial tension (right) and of the phase behavior in a ternary diagram (left) along a formulation unidimensional scan (here, the salinity of the aqueous phase S). S* and γ* are the salinity and the interfacial tension at optimum formulation, respectively.

3. Multivariable Scans and Generalized HLD Expression for Optimum Formulation

Figure 3 displays the phase behavior transitions in the two-dimensional S-ACN space when all other variables are constant. In the left plot, numerical values are indicated in the ordinate for salinity and in abscissa for ACN. The gray area indicates the three-phase zone (WIII). A vertical variation of salinity at the ACN constant corresponds to **Figure 2** salinity scan, while a horizontal variation of ACN at constant salinity is an ACN scan. The line at the center of the three-phase zone is the optimum formulation line in a bidimensional scan; it corresponds to the optimum ACN* at constant salinity and to the optimum S* at constant ACN. Hence, an increase in salinity results in the transition WI > WIII > WII, while an increase in ACN does the opposite. **Figure 3** corresponds to a typical system for EOR, containing 1 wt% of a commercial alkylbenzene sulfonate with 3 vol% of 2-butanol co-surfactant at a fixed temperature and pressure. It can be seen in **Figure 3** (right plot) that the optimum formulation line at the center of the three-phase zone becomes exactly a straight line if the LnS scale is used in the ordinate.

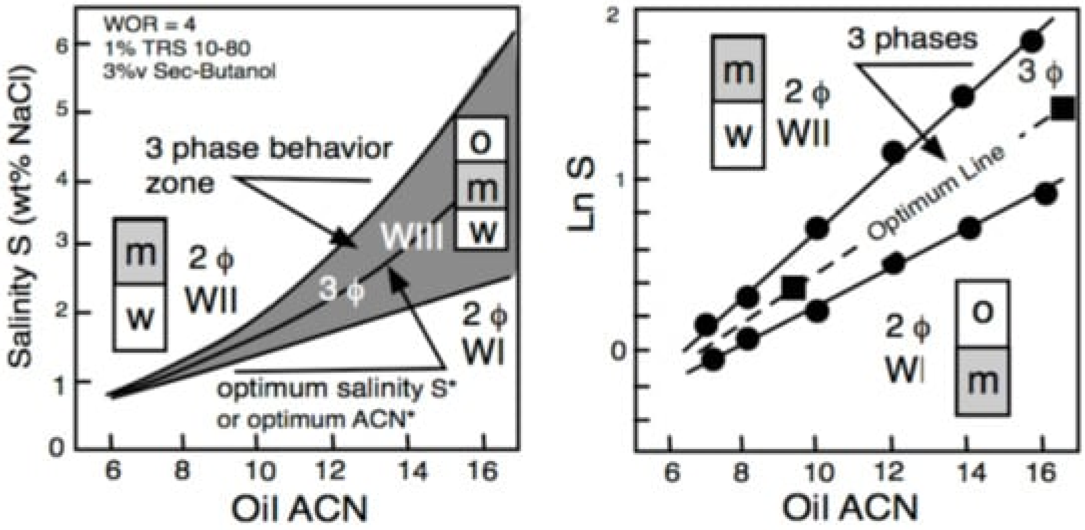

Figure 3. Bidimensional (water salinity and oil ACN) formulation scan [5]. S* is the salinity at optimum ormulation.

Consequently, the equation of the optimum formulation line in this LnS-ACN space may be written as LnS = K_A ACN + CST, where the constant term (CST) depends on the other variables that do not change, i.e., the surfactant and cosurfactant, the temperature and the pressure. Such a bidimensional variation of both oil ACN and water salinity (for instance, between the two square dots located on the optimum line) may be expressed as ΔHLD = ΔLnS − K_A ΔACN = 0 at all other constant variables.

Numerous studies from various laboratories in the past 40 years [24][47][52][53][54][55][56] indicated that this linear relationship is essentially valid (at least over some range of ACN of about 10 units for all ionic surfactants). However, the ACN coefficient K_A value was found to depend on the surfactant, particularly its head group. It is 0.16 for alkylbenzene sulfonate, 0.10 for *n*-alkyl sulfate or carboxylate, 0.17 for the dihexylsulfosuccinate, and 0.20 for alkyl trimethyl ammonium salts. For extended surfactants with several blocks, such as the alkyl polypropoxy ethoxy sulfates or carboxylates, this K_A coefficient is particularly low, i.e., 0.05 to 0.10, and depends on the exact structure—in particular, the alkoxylated central block size [2].

A slight departure from linearity with LnS has been found for complex head groups, mainly when there is an internal or external mixture of ionic and nonionic parts [6][14][57]. A linear relation between S (instead of LnS) and ACN generally better matches ethoxylated nonionic surfactant [47][58]. However, the effect is much weaker than for ionic species and a partitioning inconvenience occurs with commercial surfactants, affecting the numerical data accuracy.

This double scan technique with an exact compensation of two opposite effects was introduced by the University of Texas group in 1977 and was later applied to many different pairs of variables susceptible to altering the interactions of the surfactant with both oil and water. The equations summarized in **Table 2** indicate numerical results from a double scan change involving two variables, i.e., $\Delta HLD = 0$, from our data and other publications cited in the two previous paragraphs.

Table 2. Different cases of equations indicating the changes of two formulation variables to deviate from optimum formulation and to return to it ($\Delta HLD = 0$) with coefficients found in experimental data.

HLD Equation–Surfactant Type
$\Delta HLD_1 = \Delta LnS - 0.16\ \Delta ACN = 0$ for alkylbenzene sulfonates $\Delta HLD_2 = \Delta LnS - 0.19\ \Delta ACN = 0$ for alkyltrimethyl ammonium chlorides $\Delta HLD_3 = \Delta LnS - 0.07\ \Delta ACN = 0$ for alkyl hexapropyleneoxide diethylenoxide sulfates $\Delta HLD_4 = 0.33\ \Delta SAT - \Delta EON = 0$ for ethoxylated *n*-alcohol with EON~5 and T~25 °C $\Delta HLD_5 = 0.13\ \Delta S - \Delta EON = 0$ for ethoxylated *n*-alcohol with EON~5 and T~25 °C $\Delta HLD_6 = 2.25\ \Delta SAT - \Delta ACN = 0$ for ethoxylated *n*-alcohol with EON~5 $\Delta HLD_7 = -\ 0.24\ \Delta ACN - \Delta EON = 0$ for ethoxylated *n*-alcohol with EON~5 $\Delta HLD_8 = -\ \Delta T - 20\ \Delta ACN = 0$ for *n*-alkyl sulfates $\Delta HLD_9 = -\ \Delta T - 14.3\ \Delta ACN = 0$ for alkylbenzene sulfonates $\Delta HLD_{10} = \Delta T - 4\ \Delta ACN = 0$ for ethoxylated nonionic (EON~5–6 & T~20–30 °C) $\Delta HLD_{11} = \Delta T - 1.4\ \Delta ACN = 0$ for ethoxylated nonionic (EON~8–9 & T~70 °C) $\Delta HLD_{12} = \Delta T - 0.90\ \Delta ACN = 0$ for ethoxylated nonionic (EON~10–11 & T~80–90 °C) $\Delta HLD_{13} = -\ \Delta GN - 0.12\ \Delta ACN = 0$ for polyglyceryl monolaurate (GN~5–6) $\Delta HLD_{14} = \Delta LnS - 0.14\ \Delta PON = 0$ for alkyl polypropyleneoxide diethylenoxide sulfates

where S is the salinity in wt% NaCl, EON is the exact or average number of ethylene oxide groups, SAT is the surfactant n-alkyl tail length in carbon atom number, T is the temperature in °C, and GN is the number of glyceryl group in polyglyceryl monolaurate oligomers.

3.1. The Normalized Hydrophilic Lipophilic Deviation (HLD_N) Equation

The previous data comes from many different experiments. It should be noted that the numerical values of the equivalence of the change between two variables are arbitrarily written as $K_1\ \Delta V_1 - K_2\ \Delta V_2 = 0$, which could be systematically written as $\Delta V_1 = K_{21}\ \Delta V_2$ with the coefficient $K_{21} = K_2/K_1$, as the linear equivalence in the ΔHLD double change.

The proper variable to make a comparison between different cases is to have the same change, which has been recently taken as a unit change in ACN, which is the same in all the cases [9][11]. Consequently, the previous list of equations on $\Delta HLD = 0$ will be divided by the coefficient before ACN, so that in the “normalized” expression, it would become −1 as in **Table 3** ΔHLD_{Ni} Equations (1)–(3). The minus sign is explained by the fact that an increase in ACN tends to decrease the numerator of R, thus reducing the HLD.

Table 3. Various cases of equations indicating the changes of two formulation variables to deviate from optimum formulation and return to it ($\Delta HLD = 0$) with the same −1 coefficient in front of the ΔACN so that all the equations have the same scale.

HLD_N Equation−Surfactant Type
$\Delta HLD_{N1} = 6.25\ \Delta LnS - \Delta ACN = 0$ for alkylbenzene sulfonates
$\Delta HLD_{N2} = 5.26\ \Delta LnS - \Delta ACN = 0$ for alkyltrimethyl ammonium chlorides
$\Delta HLD_{N3} = 14.3\ \Delta LnS - \Delta ACN = 0$ for alkyl hexapropyleneoxide diethylenoxide sulf.
$\Delta HLD_{N4} = 1.4\ \Delta SAT - 4.2\ \Delta EON = 0$ for ethoxylated *n*-alcohol (EON~5 & T~25 °C)
$\Delta HLD_{N5} = 0.55\ \Delta S - 4.2\ \Delta EON = 0$ for ethoxylated *n*-alcohol (EON~5 & T~25 °C)
$\Delta HLD_{N6} = 2.25\ \Delta SAT - \Delta ACN = 0$ for ethoxylated *n*-alcohol with EON~5
$\Delta HLD_{N7} = -\ 4.2\ \Delta EON - \Delta ACN = 0$ for ethoxylated *n*-alcohol with EON~5
$\Delta HLD_{N8} = -\ 0.05\ \Delta T - \Delta ACN = 0$ for *n*-alkyl sulfates
$\Delta HLD_{N9} = -\ 0.07\ \Delta T - \Delta ACN = 0$ for alkylbenzene sulfonates
$\Delta HLD_{N10} = 0.25\ \Delta T - \Delta ACN = 0$ for ethoxylated nonionic (EON~5–6 & T~20–30 °C)
$\Delta HLD_{N11} = 0.70\ \Delta T - \Delta ACN = 0$ for ethoxylated nonionic (EON~8–9 & T~70 °C)
$\Delta HLD_{N12} = 1.1\ \Delta T - \Delta ACN = 0$ for ethoxylated nonionic (EON~11 & T~80–90 °C)
$\Delta HLD_{N13} = -\ 8.3\ \Delta GN - \Delta ACN = 0$ for polyglyceryl monolaurate (GN~5–6)
$\Delta HLD_{N14} = 1.2\ \Delta PON - \Delta ACN = 0$ for alkyl polypropyleneoxide PON sulfates

Thus, all the previous equations will be written as follows with the properly evaluated or calculated K_i coefficient before any V_i variable. The normalized equation implies ACN and at least one V_i variable to produce the double scan compensation but can include 3, 4, 5, etc.

$$\Delta HLD_N = 1 - 1 = 0 = -\ \Delta ACN + \sum \pm K_i\ \Delta V_i \text{ with } i = 2, 3, 4 \text{ etc.} \qquad (1)$$

If the double change does not include a unit variation of ΔACN, it should include variations of (at least) two other variables that are equivalent to $\Delta ACN = \pm 1$, as in the ΔHLD_{Ni} equations numbers 4, 5, in the previous list, which indicate the proper coefficient K_i before all formulation variables.

The data displayed in **Table 3** deserve some specific comments. When a − ΔACN term appears in one of the equations, a positive effect of another term indicates that the corresponding variable change increases the HLD. It means that it is increasing the interaction of the surfactant with oil or diminishing its interaction with water by an amount equivalent to a negative unit of ACN. Therefore, from the previous **Table 3** data, diminishing the ACN by one unit has the same effect as adding 0.44 carbon atoms in the surfactant *n*-alkyl tail (SAT) or adding 0.83 propylene oxide group (PON) in the intermediate part of an alkyl polypropoxy extended surfactant, or removing 0.24 ethylene oxide group from the head (EON) of an ethoxylated alcohol.

Transforming expression (2) to a differential equation level and taking into account that the first partial derivatives are constant (over some range) [10][11]

$$dHLD_N = 0 = -dACN + \sum \pm K_i\ \Delta dV_i \text{ with } i = 2, 3, 4 \text{ etc.} \qquad (2)$$

and integrating it

$$HLD_N = 0 = -(ACN - ACNref) + \sum \pm Ki\ (Vi - Vi\ ref) \text{ with } i = 2, 3, 4 \text{ etc.} \qquad (3)$$

Including an integration constant which is zero when all the variables are at a reference in which there is an optimum formulation.

Using only four variables to describe a simple system, i.e., surfactant, oil, water and temperature, the equation $HLD_N = 0$ at optimum formulation can be written as follows for ionic and nonionic surfactants [9]:

$$HLD_N = K_S\,(LnS/S_{ref}) - (ACN - ACN_{ref}) - K_{TIO}\,(T - T_{ref}) + SCP_N - SCP_{Nref}\ \text{(ionic)} \qquad (4)$$

$$HLD_N = K_S\,(S - S_{ref}) - (ACN - ACN_{ref}) + K_{TNI}\,(T - T_{ref}) + SCP_N - SCP_{Nref}\ \text{(nonionic)} \qquad (5)$$

In the past few years and with or without clear explanations, the references have been taken as follows. $S_{ref} = 1$, because ionic surfactants are salts that thus provide a minimum salinity or equivalent salinity in wt% NaCl, which is in general much smaller than 1 wt% [59]. What is favorable is that, consequently, LnS_{ref} becomes zero in the ionic surfactant equation. A Sref = 0 often provides the reference for nonionic surfactants, but it is unfortunately different from the ionic case. Thus, it might be more logical to use $S_{ref} = 1$ in all the cases, the term K_S S_{ref} being almost negligible in most cases. $ACN_{ref} = 0$ also simplifies the equations, even if it is not a very logical choice, since it corresponds to no carbon atom in the *n*-alkane, i.e., something which does not exist. However, an equivalent EACN = 0 was found to be some approximation for benzene [60]. The temperature reference is often taken as 25 °C, but also at T = 0 °C, which simplifies the equation. This occurs even though it often corresponds to a solid-state of oil. In this simplified equation, there is no particular term for the pressure effect nor for a co-surfactant, initially called f(A) [52]; however, if this is so, the references would be the atmospheric pressure and the absence of co-surfactant.

3.2. The Normalized Surfactant Characteristic Parameter (SCP_N)

The SCP_N abbreviation means the normalized surfactant contribution term [9][11], also called σ/K_A for ionic and β/K_A for nonionics in the literature [5][52][61], including a very comprehensive recent review [48]. To avoid confusion, the SCP_{ref} term is always taken as zero. However, it could be a misleading value when it is related to a characteristic surfactant curvature since it depends on many aspects other than the surfactant [10][62]. The term SCP_N changes with the surfactant, i.e., it increases by 2.26 when a carbon atom is added to its *n*-alkyl tail, and it decreases by 6.67 when an EON group is added to its polyethoxylated head). Then, its value depends on the references for all the variables, which is the reason why it is not a surfactant characteristic.

$HLD_N = 0$ equation makes it possible to numerically express the conditions for an optimum formulation in the same scale (ΔACN unit change). It thus allows to make comparisons between the corresponding SCP_N values for various surfactants, and it also makes it possible to calculate the values of mixtures according to

$$HLD_{Nmix} = \sum X_i\ HLD_{Ni}\ \text{or}\ SCP_{Nmix} = \sum Xi\ SCP_{Ni} \qquad (6)$$

With X indicating the molar fraction at the interface, which is often approximated as the weight fraction in the system, although such linearity could be erroneous in the presence of partitioning of the different species, as in many commercial surfactants. [63][60][64][65].

4. Lipophilic and Hydrophilic Linkers, and Extended Surfactants

4.1. The Lipophilic Linker

Since the main difficulty was to increase the interaction on the oil side, a special C1 highly lipophilic amphiphile was used to replace the C1 surfactant, as indicated in **Figure 4**b, while the C2 surfactant was only slightly hydrophilic, and thus was likely to mainly go to the interface. This C1 species was typically a *n*-decanol or dodecanol that was not really a surfactant adsorbed at interface but rather a polar oil segregated in the oil phase close to the interface because of the affinity of the OH end group with water [66].

This kind of substance was called a lipophilic linker [67][68][69][70][71] because it was not a co-surfactant (since it was not adsorbed at the interface) but was a species of the oil phase staying close to the interface, as shown in **Figure 4**b. As a consequence of its location, the lipophilic linker was more or less sticking to the surfactant tail and somehow extending it further in the oil phase. Therefore, it was increasing the interaction on the oil side, and thus improving the performance.

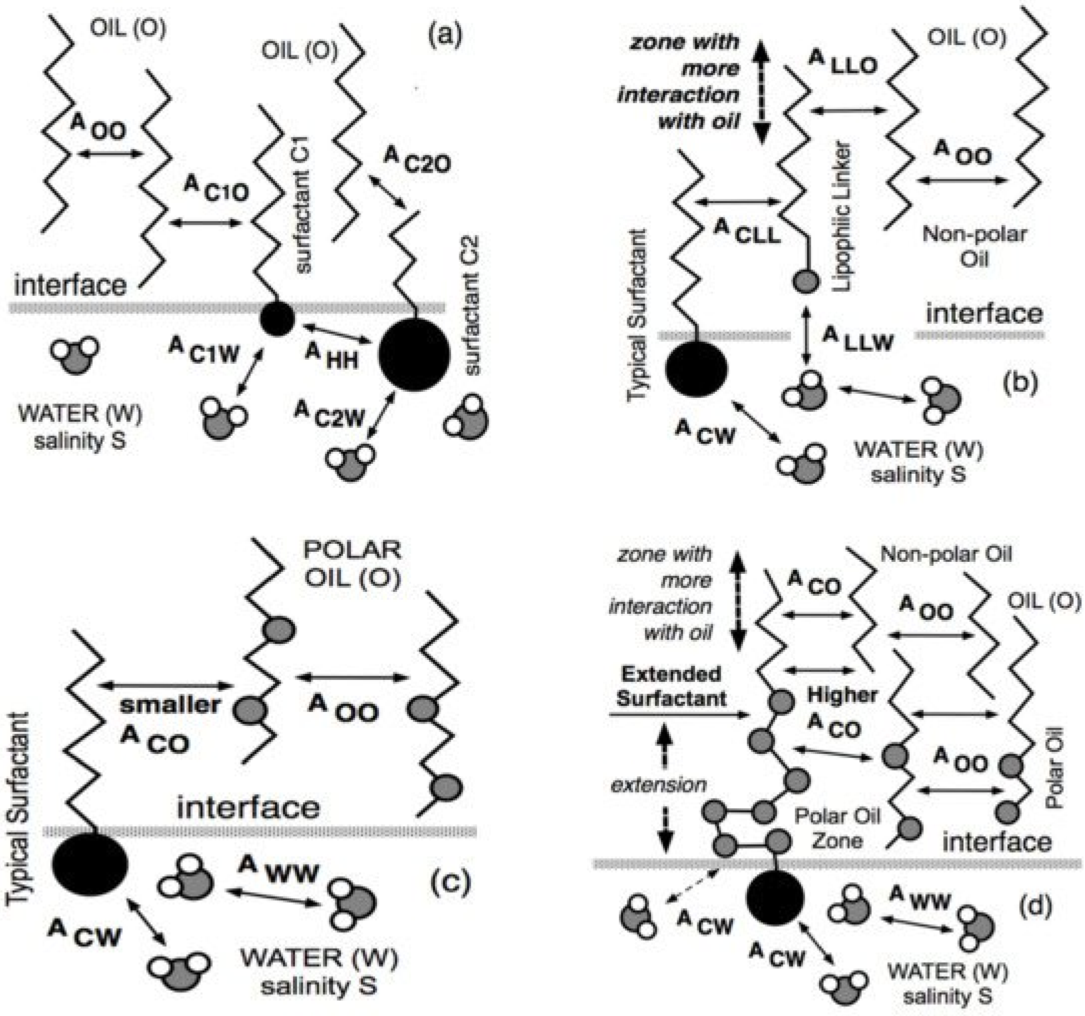

Figure 4. Interfacial arrangements (**a**) with two ordinary surfactants C1 and C1, (**b**) with a surfactant and a lipophilic linker, (**c**) with an ordinary surfactant and a polar oil, and (**d**) with an extended surfactant and a polar oil.

4.2. The Hydrophilic Linker

It was suggested that a similar intermediate be placed on the other side of the interface between the surfactant head and the water and was called a hydrophilic linker [72][73]. Its benefit was, however, much less significant, mainly because it was not producing a much higher penetration of the surfactant head group into water.

Moreover, it was known that the solubilization of a polar oil with an ordinary surfactant having a head group and an alkyl tail, as indicated in **Figure 4**c, was not very good because of a lack of perfect matching of the hydrocarbon tail with the polar oil. This is why adding a lipophilic linker in the oil phase close to the interface produced an improvement of the interaction with polar oil.

Nevertheless, the lipophilic linker was actually an oil phase component; a significant amount of it was lost in the oil bulk far from the interface, and thus partitioning was even worse with a polar oil. It was thus necessary to find a means to cumulate the favorable effects and avoid the unwanted ones.

4.3. The Extended Surfactant with an Intramolecular PO Extension

The idea developed in the 1990s [13][15][53][74] was to fasten together the rather hydrophilic surfactant and the lipophilic linker, producing the same effect as the mixture without losing a part of the lipophilic linker deviating from the interface. Since the lipophilic linker was an amphiphile with a small hydrophilic part located close to the interface, the single structure shown in **Figure 4**d to imitate the mixture situation is a so-called "extended" surfactant. It contains a polar head located in water, then an intermediate slightly polar zone in the oil phase close to the interface, and finally, the surfactant classical hydrocarbon tail. **Figure 4**d shows that the slightly polar intermediate extension is bent and interacts with the water molecules, producing more A_{CW} interaction.

The central extension was selected to be a polypropylene oxide (PO) because it was neatly lipophilic and was thus located on the oil side of the interface with good interaction with polar oil molecules. It also perfectly plays its main role of displacing the alkyl part of the tail further away from the interface, as shown in **Figure 4**d, without the usual precipitation problem at increasing the tail size. It is worth noting that our original extended surfactants, e.g., $C_{12}PO_NEO_2SO_4^-Na^+$, had a much longer intermediate (N up 14) than the alkoxylated surfactants available at this time, which had very few units only. It should be noted that a 10-unit PO chain is about three times longer than a C12 *n*-alkyl group, so that the actual tail extension is considerable, even if it is not completely perpendicular to the interface [20][75].

The PO chain is in the zone where the polar oil molecules are segregated, while the alkyl hydrocarbon part of the tail could be far away from the interface where most of the oil could be the non-polar one. This was an extra matching situation between the surfactant tail and the oil phase containing polar molecules. Sometimes, a very short ethoxylation (2 groups) is placed at the end of the PO chain, not really as a hydrophilic linker part, but rather because it makes an easier addition of the sulfate or other hydrophilic group [17][18][19][21][22].

The improving performance with polar oil was reported first by Miñana [13][53], particularly in mixtures of extended surfactants with ordinary species that were not solubilizing at all like triglyceride vegetable oils. Most research carried out in the following years used different anionic and nonionic heads sometimes connected by two EO groups to the propoxylated extension [76].

4.4. The Increased Performance of Extended Surfactant Systems with Polar Oils and Crude Oils

The general results obtained in the last 20 years have been extensively reviewed very recently [2] and should be examined in detail because of the large amount of available data. The main aspects can be summarized as follows. First of all, the PO chain is significantly lipophilic, and only sightly hydrophilic, i.e., much less than a polyethylene oxide chain. The PO unit is three times longer than a (CH_2) methylene group in a surfactant typical *n*-alkyl tail; it thus considerably extends the surfactant penetration in oil and increases the interaction, particularly with polar oil segregated close to the interface. The first 2–4 PO groups stay close to the water phase, so the molecule is twisted in this zone, and is not really straight and perpendicular to the interface, as can be seen in **Figure 4**d [26]

[77]. In some cases, the accumulation of the PO groups outside the water can be considerable, in particular at the air surface where they are said to form rugby balls [78][79]. This arbitrary gathering of the first PO group in a short and twisted hydrated chain close to the water phase produces some disorder that helps avoiding the surfactant's rigidity and precipitation. A branched structure, such as the Guerbet double tail, was found to improve the extended surfactant interaction with oil phases, in particular with di/triglycerides [14][80]. An increasing number of PO groups from five to 15 definitively increases the performance, which practically stays constant at higher PON. A PON term may be introduced in the HLD correlation but not as a linear term since it is also dealing with the surfactant hydrophobe part length (SAT) [2][27]. A more continuous change from hydrophilic to lipophilic parts, including an intermediate with an additional butylene oxide block between the alkyl tail and the propylene oxide block, improves, even more, the performance [28]. This is probably because it results in a very wide zone with a smooth variation of hydrophilicity, which is particularly appropriate to interact with crude oils containing many polar species containing functional groups bearing nitrogen, sulfur and oxygen atoms, such as asphaltenes, naphthenic acids, etc. [81][50][51][82][83].

The last benefit found in an extended surfactant is that being an intramolecular mixture between ionic and nonionic parts, a proper adjustment of the different blocks could present new opportunities such as insensitivity to temperature [84][85] or insensitivity to surfactant concentration [25] and robustness to electrolyte concentration and mixture variations, including new applications with complex biobased polar oils [29][86][87].

References

1. Salager, J.-L.; Antón, R.E.; Sabatini, D.A.; Harwell, J.H.; Acosta, E.; Tolosa, L.I. Enhancing solubilization in microemulsions-State of the art and current trends. J. Surfactants Deterg. 2005, 8, 3.
2. Salager, J.-L.; Forgiarini, A.; Marquez, R. Extended Surfactants Including an Alkoxylated Central Part Intermediate Producing a Gradual Polarity Transition—A Review of the Properties Used in Applications Such as Enhanced Oil Recovery and Polar Oil Solubilization in Microemulsions. J. Surfactants Deterg. 2019, 22.
3. Bourrel, M.; Lipow, A.M.; Wade, W.H.; Schechter, R.S.; Salager, J.-L. Properties Of Amphiphile/Oil/Water Systems At An Optimum Formulation For Phase Behavior. In Proceedings of the SPE Annual Fall Technical Conference and Exhibition, Houston, TX, USA, 1–3 October 1978.
4. Doe, P.; El-Emary, M.; Wade, W.H.; Schechter, R.S. Surfactants for producing low interfacial tensions I: Linear alkyl benzene sulfonates. J. Am. Oil Chem. Soc. 1977, 54, 570–577.
5. Salager, J.-L. Physico-Chemical Properties of Surfactant-Water-Oil Mixtures: Phase Behavior, Micro-Emulsion Formation and Interfacial Tension. Ph.D. Thesis, The University of Texas at Austin, Austin, TX, USA, 1977.

6. Carmona, I.; Schechter, R.S.; Wade, W.H.; Weerasooriya, U. Ethoxylated Oleyl Sulfonates As Model Compounds for Enhanced Oil Recovery. Soc. Pet. Eng. J. 1985, 25, 351–357.
7. Abe, M.; Schechter, D.; Schechter, R.S.; Wade, W.H.; Weerasooriya, U.; Yiv, S. Microemulsion formation with branched tail polyoxyethylene sulfonate surfactants. J. Colloid Interface Sci. 1986, 114, 342–356.
8. Maerker, J.M.; Gale, W.W. Surfactant flood process design for Loudon. SPE Reserv. Eng. 1992, 7, 36–44.
9. Salager, J.-L. A normalized Hydrophilic-Lipophilic Deviation expression HLDN is necessary to avoid confusions close to the optimum formulation of Surfactant-Oil-Water systems. J. Surfactants Deterg. 2021.
10. Salager, J.-L.; Forgiarini, A.M.; Bullón, J.; Marquez, R.; Alvarado, J.G. A Review on the Surfactant Characteristic Parameter used in Enhanced Oil Recovery, Crude Oil Dehydration and Other Formulation Applications. FIRP Booklet E729B. 2014. Available online: (accessed on 20 May 2021).
11. Salager, J.-L.; Antón, R.E.; Bullón, J.; Forgiarini, A.; Marquez, R. How to Use the Normalized Hydrophilic-Lipophilic Deviation (HLDN) Concept for the Formulation of Equilibrated and Emulsified Surfactant-Oil-Water Systems for Cosmetics and Pharmaceutical Products. Cosmetics 2020, 7, 57.
12. Baran, J.R.; Pope, G.A.; Wade, W.H.; Weerasooriya, V. Phase Behavior of Water/Perchloroethylene/Anionic Surfactant Systems. Langmuir 1994, 10, 1146–1150.
13. Miñana-Perez, M.; Graciaa, A.; Lachaise, J.; Salager, J.-L. Solubilization of polar oils with extended surfactants. Colloids Surf. A Physicochem. Eng. Asp. 1995, 100, 217–224.
14. Aoudia, M.; Wade, W.H.; Weerasooriya, V. Optimum microemulsions formulated with propoxylated Guerbet alcohol and propoxylated tridecyl alcohol sodium sulfates. J. Dispers. Sci. Technol. 1995, 16, 115–135.
15. Minana-Perez, M.; Graciaa, A.; Lachaise, J.; Salager, J.L. Systems containing mixtures of extended surfactants and conventional nonionics. Phase behavior and solubilization in microemulsion. In Proceedings of the 4th World Surfactants Congress, Barcelona, Spain, 3–7 June 1996; Volume 2, pp. 226–234.
16. Pérez, M.M.; Salager, J.-L.; Graciaa, A.; Lachaise, J. Solubilization of polar oils in microemulsion systems. Trends Colloid Interface Sci. IX 1995, 177–179.
17. Scorzza, C.; Godé, P.; Goethals, G.; Martin, P.; Miñana-Pérez, M.; Salager, J.L.; Usubillaga, A.; Villa, P. Another new family of “extended” glucidoamphiphiles. Synthesis and surfactant properties for different sugar head groups and spacer arm lengths. J. Surfactants Deterg. 2002, 5, 337–343.

18. Scorzza, C.; Godé, P.; Martin, P.; Miñana-Pérez, M.; Salager, J.L.; Villa, P.; Goethals, G. Synthesis and surfactant properties of a new “extended” glucidoamphiphile made from D-glucose. J. Surfactants Deterg. 2002, 5, 331–335.
19. Goethals, G.; Fernández, A.; Martin, P.; Miñana-Pérez, M.; Scorzza, C.; Villa, P.; Godé, P. Spacer arm influence on glucidoamphiphile compound properties. Carbohydr. Polym. 2001, 45, 147–154.
20. Salager, J.; Scorzza, C.; Forgiarini, A.; Arandia, M.A.; Pietrangeli, G.; Manchego, L.; Vejar, F. Amphiphilic Mixtures versus Surfactant Structures with Smooth Polarity Transition across Interface to Improve Solubilization Performance. In Proceedings of the CESIO 2008—7th World Surfactant Congress Paris Session: Design and Analisis—Paper Number O-A17, Paris, France, 22–25 June 2008; pp. 1–9.
21. Fernández, A.; Scorzza, C.; Usubillaga, A.; Salager, J.-L. Synthesis of new extended surfactants containing a carboxylate or sulfate polar group. J. Surfactants Deterg. 2005, 8, 187–191.
22. Fernández, A.; Scorzza, C.; Usubillaga, A.; Salager, J. Synthesis of new extended surfactants containing a xylitol polar group. J. Surfactants Deterg. 2005, 8, 193–198.
23. Illous, E.; Ontiveros, J.F.; Lemahieu, G.; Lebeuf, R.; Aubry, J.M. Amphiphilicity and salt-tolerance of ethoxylated and propoxylated anionic surfactants. Colloids Surf. A Physicochem. Eng. Asp. 2020, 601, 124786.
24. Velásquez, J.; Scorzza, C.; Vejar, F.; Forgiarini, A.M.; Antón, R.E.; Salager, J.L. Effect of temperature and other variables on the optimum formulation of anionic extended surfactant-alkane-brine systems. J. Surfactants Deterg. 2010, 13, 69–73.
25. Arandia, M.A.; Forgiarini, A.M.; Salager, J.-L. Resolving an enhanced oil recovery challenge: Optimum formulation of a surfactant-oil-water system made insensitive to dilution. J. Surfactants Deterg. 2010, 13, 119–126.
26. Forgiarini, A.M.; Scorzza, C.; Velásquez, J.; Vejar, F.; Zambrano, E.; Salager, J. Influence of the mixed propoxy/ethoxy spacer arrangement order and of the ionic head group nature on the adsorption and aggregation of extended surfactants. J. Surfactants Deterg. 2010, 13, 451–458.
27. Solairaj, S.; Britton, C.; Lu, J.; Kim, D.H.; Weerasooriya, U.; Pope, G.A. New correlation to predict the optimum surfactant structure for EOR. In Proceedings of the SPE—DOE Improved Oil Recovery Symposium, Tulsa, OK, USA, 14–18 April 2012; Volume 2, pp. 1390–1399.
28. Yang, H.; Britton, C.; Liyanage, P.J.; Solairaj, S.; Kim, D.H.; Nguyen, Q.; Weerasooriya, U.; Pope, G.A. Low-cost, high-performance chemicals for enhanced oil recovery. Proceedings SPE—DOE Improved Oil Recovery Symposium, Tulsa, OK, USA, 24–28 April 2010; Volume 2, pp. 1474–1497.
29. Phaodee, P.; Sabatini, D.A. Effect of Surfactant Systems, Alcohol Types, and Salinity on Cold-Water Detergency of Triacylglycerol Semisolid Soil. Part II. J. Surfactants Deterg. 2020, 23, 423–

432.

30. Witthayapanyanon, A.; Acosta, E.; Harwell, J.H.; Sabatini, D.A. Formulation of ultralow interfacial tension systems using extended surfactants. J. Surfactants Deterg. 2006, 9, 331–339.
31. Salager, J.L.; Forgiarini, A.M.; Antón, R.E.; Quintero, L. Available know-how in transforming an emulsified drilling fluid to be removed from an unwanted location into a low-viscosity single-phase system. Energy Fuels 2012, 26, 4078–4085.
32. Quintero, L.; Clark, D.E.; Salager, J.; Forgiarini, A. Mesophase Fluids with Extended Chain Surfactants for Downhole Treatments. US Patent Office US8235120B2, 7 August 2012.
33. Quintero, L.; Clark, D.E.; Cardenas, A.E.; Salager, J.; Forgiarini, A.; Bahsas, A.H. Dendritic Surfactants and Extended Surfactants for Drilling Fluid Formulations. US Patent Office US20120241220A1, 27 September 2012.
34. Delgado-Linares, J.G.; Pereira, J.C.; Rondón, M.; Bullón, J.; Salager, J.L. Breaking of Water-in-Crude Oil Emulsions. 6. Estimating the Demulsifier Performance at Optimum Formulation from Both the Required Dose and the Attained Instability. Energy Fuels 2016, 30, 5483–5491.
35. Pereira, J.C.; Delgado-Linares, J.; Scorzza, C.; Rondón, M.; Rodríguez, S.; Salager, J.-L. Breaking of Water-in-Crude Oil Emulsions. 4. Estimation of the Demulsifier Surfactant Performance To Destabilize the Asphaltenes Effect. Energy Fuels 2011, 25, 1045.
36. Marquez, R.; Forgiarini, A.; Langevin, D.; Salager, J.-L. Breaking of Water-In-Crude Oil Emulsions. Part 9. New Interfacial Rheology Characteristics Measured Using a Spinning Drop Rheometer at Optimum Formulation. Energy Fuels 2019, 33, 8151–8164.
37. Roon, L.; Oesper, R.E. A Contribution to the Theory of Emulsification Based on Pharmaceutical Practice. Ind. Eng. Chem. 1917, 9, 156–161.
38. Crockett, W.G.; Oesper, R.E. A Contribution to the Theory of Emulsification Based on Pharmaceutical Practice-II. Ind. Eng. Chem. 1917, 9, 967–969.
39. Harkins, W.D.; McLaughlin, H.M. The structure of films of water on salt solutions I. Surface tension and adsorption for aqueous solutions of sodium chloride. J. Am. Chem. Soc. 1925, 47, 2083–2089.
40. Griffin, W. Classification of surface-active agents by “HLB”. J. Soc. Cosmet. Chem. 1949, 1, 311–326.
41. Griffin, W. Calculation of HLB Values of Non-ionic Surfactants. J. Soc. Cosmet. Chem. 1954, 5, 249.
42. Becher, P. Emulsions: Theory and Practice; Oxford University Press: New York, NY, USA, 2001; ISBN 0-8412-3496-5.

43. Winsor, P. Hydrotropy, solubilisation and related emulsification processes. Trans. Faraday Soc. 1948, 44, 376–398.
44. Winsor, P. Solvent Properties of Amphiphilic Compounds; Butterworths Scientific Publications: Oxford, UK, 1954.
45. Winsor, P. Binary and multicomponent solutions of amphiphilic compounds. Solubilization and the formation, structure, and theoretical significance of liquid crystalline solutions. Chem. Rev. 1968, 68, 1–40.
46. Bourrel, M.; Verzaro, F.; Chambu, C. Effect of Oil Type on Solubilization by Amphiphiles. SPE Reserv. Eng. 1987, 2, 41–53.
47. Bourrel, M.; Schechter, R.S. Microemulsions and Related Systems: Formulation, Solvency, and Physical Properties; Editions Technip: Paris, France, 2010; ISBN 2710809567.
48. Salager, J.-L.; Forgiarini, A.M.; Bullón, J. How to attain ultralow interfacial tension and three-phase behavior with surfactant formulation for enhanced oil recovery: A review. Part 1. Optimum formulation for simple surfactant-oil-water ternary systems. J. Surfactants Deterg. 2013, 16, 449–472.
49. Ghosh, S.; Johns, R.T. Dimensionless Equation of State to Predict Microemulsion Phase Behavior. Langmuir 2016, 32, 8969–8979.
50. Fotland, P.; Skange, A. Ultralow Interfacial Tension as a Function of Pressure. J. Dispers. Sci. Technol. 1986, 7, 563.
51. Austad, T.; Strand, S. Chemical flooding of oil reservoirs 4. Effects of temperature and pressure on the middle phase solubilization parameters close to optimum flood conditions. Colloids Surf. A Physicochem. Eng. Asp. 1996, 108, 243–252.
52. Salager, J.-L.; Morgan, J.C.; Schechter, R.S.; Wade, W.H.; Vasquez, E. Optimum formulation of surfactant/water/oil systems for minimum interfacial tension or phase behavior. Soc. Pet. Eng. J. 1979, 19, 107–115.
53. Salager, J.L. Quantifying the concept of physico-chemical formulation in surfactant-oil-water systems—state of the art. Trends Colloid Interface Sci. X 1996, 137–142.
54. Antón, R.E.; Garcés, N.; Yajure, A. A correlation for three-phase behavior of cationic surfactant-oil-water systems. J. Dispers. Sci. Technol. 1997, 18, 539–555.
55. Hammond, C.E.; Acosta, E.J. On the characteristic curvature of alkyl-polypropylene oxide sulfate extended surfactants. J. Surfactants Deterg. 2012, 15, 157–165.
56. Nguyen, T.T.; Morgan, C.; Poindexter, L.; Fernandez, J. Application of the Hydrophilic–Lipophilic Deviation Concept to Surfactant Characterization and Surfactant Selection for Enhanced Oil Recovery. J. Surfactants Deterg. 2019, 22, 983–999.

57. Barakat, Y.; Fortney, L.N.; Schechter, R.S.; Wade, W.H.; Yiv, S.H.; Graciaa, A. Criteria for structuring surfactants to maximize solubilization of oil and water: II. Alkyl benzene sodium sulfonates. J. Colloid Interface Sci. 1983, 92, 561–574.
58. Bourrel, M.; Salager, J.-L.; Schechter, R.S.; Wade, W.H. A correlation for phase behavior of nonionic surfactants. J. Colloid Interface Sci. 1980, 75, 451–461.
59. Antón, R.E.; Salager, J.-L. Effect of the Electrolyte Anion on the Salinity Contribution to Optimum Formulation of Anionic Surfactant Microemulsions. J. Colloid Interface Sci. 1990, 140, 75.
60. Aubry, J.M.; Ontiveros, J.F.; Salager, J.-L.; Nardello-Rataj, V. Use of the normalized hydrophilic-lipophilic-deviation (HLDN) equation for determining the equivalent alkane carbon number (EACN) of oils and the preferred alkane carbon number (PACN) of nonionic surfactants by the fish-tail method (FTM). Adv. Colloid Interface Sci. 2020, 276.
61. Salager, J.-L.; Bourrel, M.; Schechter, R.S.; Wade, W.H. Mixing Rules for Optimum Phase Behavior Formulation of Surfactant-Oil-Water Systems. Soc. Pet. Eng. J. 1979, 19, 271.
62. Acosta, E.; Yuan, J.S.; Bhakta, A.S. The characteristic curvature of ionic surfactants. J. Surfactants Deterg. 2008, 11, 145.
63. Salager, J.-L.; Marquez, N.; Graciaa, A.; Lachaise, J. Partitioning of ethoxylated octylphenol surfactants in microemulsion-oil-water systems: Influence of temperature and relation between partitioning coefficient and physicochemical formulation. Langmuir 2000, 16, 5534–5539.
64. Marquez, N.; Anton, R.E.; Graciaa, A.; Lachaise, J.; Salager, J.L. Partitioning of ethoxylated alkylphenol surfactants in microemulsion-oil-water systems. Colloids Surf. A Physicochem. Eng. Asp. 1995, 100, 225–231.
65. Márquez, N.; Anton, R.E.; Graciaa, A.; Lachaise, J.; Salager, J.-L. Partitioning of ethoxylated alkylphenol surfactants in microemulsion- oil-water systems. Part II: Influence of hydrophobe branching. Colloids Surf. A Physicochem. Eng. Asp. 1998, 131, 45–49.
66. Graciaa, A.; Lachaise, J.; Cucuphat, C.; Bourrel, M.; Salager, J.L. Interfacial Segregation of an Ethyl Oleate/Hexadecane Oil Mixture in Microemulsion Systems. Langmuir 1993, 9, 1473–1478.
67. Graciaa, A.; Lachaise, J.; Cucuphat, C.; Bourrel, M.; Salager, J.L. Improving solubilization in microemulsions with additives. 1. The lipophilic linker role. Langmuir 1993, 9, 669–672.
68. Graciaa, A.; Lachaise, J.; Cucuphat, C.; Bourrel, M.; Salager, J.L. Improving Solubilization in Microemulsions with Additives. 2. Long Chain Alcohols as Lipophilic Linkers. Langmuir 1993, 9, 3371–3374.
69. Salager, J.L.; Graciaa, A.; Lachaise, J. Improving solubilization in microemulsions with additives. Part III: Lipophilic linker optimization. J. Surfactants Deterg. 1998, 1, 403–406.

70. Acosta, E.; Do Mai, P.; Harwell, J.H.; Sabatini, D.A. Linker-Modified Microemulsions for a Variety of Oils and Surfactants. J. Surfactants Deterg. 2003, 6, 353–363.
71. Quintero, L.; Pietrangeli, G.; Hughes, B.; Salager, J.L.; Forgiarini, A. Optimization of microemulsion formulations with linker molecules. In Proceedings of the SPE–European Formation Damage Conference, EFDC, Noordwijk, The Netherlands, 5–7 June 2013; Volume 2, pp. 1275–1287.
72. Acosta, E.; Uchiyama, H.; Sabatini, D.A.; Harwell, J.H. The role of hydrophilic linkers. J. Surfactants Deterg. 2002, 5, 151–157.
73. Frank, C.; Frielinghaus, H.; Allgaier, J.; Richter, D. Hydrophilic alcohol ethoxylates as efficiency boosters for Microemulsions. Langmuir 2008, 24, 6036–6043.
74. Miñana-Pérez, M. Contribution à la Microémulsification d'huiles Polaires de Synthèse ou Naturelles. Ph.D. Thesis, Universidad de Los Andes—Universite de Pau, Santiago, Chile, 1993.
75. Salager, J.-L.; Forgiarini, A.M. Extended surfactants A fine tuned structure to improve interfacial performance. In Proceedings of the 101st AOCS Annual Meeting, Phoenix, AZ, USA, 16–19 May 2010.
76. Salager, J.L.; Scorzza, C.; Fernandez, A.; Antón, R.E.; Miñana-Pérez, M.; Usubillaga, A.; Villa, P. Enhancing Solubilization in Microemulsions: From Classic To Novel "Extended" Surfactant Structures. In Proceedings of the Surfactants in Solution, Barcelona, Spain, 9–14 June 2002.
77. Salager, J.; Forgiarini, A.; Marquez, L. Understanding of Extended Surfactants Intramolecular Structure to enhance solubilization for a variety of applications. In Proceedings of the 8th World Surfactant Congress CESIO, Vienna, Austria, 6–8 June 2011.
78. Chen, J.; Hu, X.Y.; Fang, Y.; Liu, H.H.; Xia, Y.M. Comparative Study of Conventional/Ethoxylated/Extended n-Alkylsulfate Surfactants. Langmuir 2019, 35, 3116–3125.
79. Chen, J.; Hu, X.Y.; Fang, Y.; Jin, G.Y.; Xia, Y.M. What dominates the interfacial properties of extended surfactants: Amphipathicity or surfactant shape? J. Colloid Interface Sci. 2019, 547, 190–198.
80. Lu, J.; Britton, C.; Solairaj, S.; Liyanage, P.J.; Kim, D.H.; Adkins, S.; Arachchilage, G.W.P.; Weerasooriya, U.; Pope, G.A. Novel large-hydrophobe alkoxy carboxylate surfactants for enhanced oil recovery. SPE J. 2014, 19, 1024–1034.
81. Han, X.; Lu, M.; Fan, Y.; Li, Y.; Holmberg, K. Recent Developments on Surfactants for Enhanced Oil Recovery. Tenside Surfactants Deterg. 2021, 58, 164–176.
82. Ghosh, S.; Johns, R.T. An Equation-of-State Model To Predict Surfactant/Oil/Brine-Phase Behavior. SPE J. 2016, 21, 1106.

83. Chung, J.; Holtsclaw, J.; Henderson, T.C.; Everett, T.A.; Schultheiss, N.C.; Boudouris, B.W.; Franses, E.I. Relationship of Various Interfacial Tensions of Surfactants/Brine/Oil Formulations to Oil Recovery Efficiency. Energy Fuels 2021, 35, 7768–7777.
84. Antón, R.E.; Graciaa, A.; Lachaise, J.; Salager, J.L. Surfactant-Oil-Water Systems Near the Affinity Inversion, Part VIII: Optimum Formulation and Phase Behavior of Mixed Anionic-Nonionic Systems Versus Temperature. J. Dispers. Sci. Technol. 1992, 13, 565–579.
85. Acosta, E.; Bhakta, A.S. The HLD-NAC model for mixtures of ionic and nonionic surfactants. J. Surfactants Deterg. 2009, 12, 7–19.
86. Gagnon, Y.; Mhemdi, H.; Delbecq, F.; Van Hecke, E. Extended surfactants and their tailored applications for vegetable oils extraction: An overview. OCL Oilseeds Fats Crop. Lipids 2021, 28.
87. Salager, J.-L.; Forgiarini, A.M.; Rondón, M.J. How to Attain an Ultralow Interfacial Tension and a Three-Phase Behavior with a Surfactant Formulation for Enhanced Oil Recovery: A Review—Part 3. Practical Procedures to Optimize the Laboratory Research according to the Current State of the Art in Surf. J. Surfactants Deterg. 2017, 20, 3.

Retrieved from https://encyclopedia.pub/entry/history/show/92750